

Structure and Mechanical Properties of Nickel Electrodeposits

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ABSTRACT

Relationship of “ processing/microstructure/mechanical-properties ” of electrodeposited nickel was established to achieve better understanding of the annealing behaviors Ni deposits. 70 μ m-thick Ni was electrodeposited onto copper plates from Ni sulfamate baths with the addition of various amounts of chloride and ammonium ions. Electroplating parameters studied include solution temperature, current density and pH. Ni deposits were then annealed at temperatures ranging from 200 to 600 °C for 1hr. Optical microscopy, scanning electron microscopy, transmission electron microscopy, and x-ray diffraction technique were used to characterize the microstructure and texture of Ni deposits, particularly the grain structure and lattice defects. Fibrous structure of [110] texture was observed for Ni deposits plated from 40 °C bath at current density less than 1 A/dm². Recrystallization and grain growth occur after annealing at temperatures higher than 400 °C. Ni deposits plated at current density above 1 A/dm² show well-defined columnar grain structure with strong [100] texture. [100] oriented Ni deposits are softer and still exhibit columnar grain structure even after 600 °C annealing. Although Ni deposits plated at various current densities exhibit a bimodal grain structure, average grain size of Ni deposits increases with current density. In contrast, lattice defects of Ni deposits decreases with current density. For 40 °C baths, pH variations between 3.0 and 5.0 show little effect on the texture and structure of Ni deposits, which consist of columnar grains with [100] texture. Columnar grain structure still exists up to 600 °C annealing. Addition of ammonium and chloride ions modifies the electrocrystallization and growth of Ni deposits. For 40 °C bath, texture of Ni deposits change from strong [100] to weak [100], and then to weak [110] with the increase of ammonium ions in the bath. With the addition of 100 ppm ammonium ions into 50 °C bath, Ni deposits exhibit a mixture of [110] and [310] textures. Ni deposits with [110] and/or [310] textures suffer recrystallization after 400 °C annealing. Addition of 30g/l NiCl₂·6H₂O into 40 °C bath results in the texture change from [100] to weak [100]. [110] oriented Ni deposits are plated from 50 °C bath with the addition of 3 ~ 60g/l NiCl₂·6H₂O. Recrystallization of Ni deposits with weak [100] orientation and with [110] orientation occur after 400 °C annealing. In general, Ni deposits with inhibition textures, such as [110] and [310], tend to recrystallize after 400 °C annealing. In contrast, strongly [100] oriented Ni deposits still exhibit columnar grain structure even after 600 °C annealing.

Keywords : 胺基磺酸鎳浴 ; 穿透式電子顯微鏡 ; 纖維晶 ; 再結晶與晶粒成長 ; 柱狀晶 ; 優選方位

Table of Contents

封面內頁 簽名頁 授權書.....	iii	中文摘要.....	iii
.....v	英文摘要.....vii	誌謝.....
.....ix	目錄.....x	圖目錄.....
.....xiv	表目錄.....xxiv	第一章 導論.....
.....1	1.1 前言.....1	1.2 研究動機.....
.....2	第二章 文獻探討.....44
2.1 電化學反應.....	4.2 鍍鎳溶液種類.....44
2.3 電鍍鎳液中的不純物.....	5.2 鍍層的內應力.....77
2.5 鍍層的硬度.....	9.2 鍍層的結構.....1313
2.7 鍍層的織構或優選方位.....	17	第三章 實驗方法.....17
.....20	3.1 電鍍設備.....	20.2 鍍鎳層的製備.....20
.....21	3.2.1 鍍液的化學成分.....	21.3.2 銅底材.....21
.....27	3.2.3 鎳圓塊.....	28.3.2.4 操作條件.....28
.....28	3.2.5 銅底材前處理.....	29.3.2.6 熱處理.....29
.....30	3.2.7 試片編號.....	31.3.3 鍍鎳銅底材機械性質量測.....31
.....32	3.3.1 微硬度試驗.....	32.3.3.2 高溫磨耗試驗.....32
.....33	3.3.4 微觀組織試片製作與觀察.....	35.3.4.1 光學顯微鏡試片準備.....35
.....35	3.4.2 掃描式電子顯微鏡試片製作與觀察.....	36.3.4.3 穿透式電子顯微鏡試片製作與觀察.....36
.....37	3.4.4 X光繞射.....	39	第四章 實驗結果.....

.....45 4.1 電流密度的影響.....	45 4.1.1 XRD組織觀察.....
.....45 4.1.2 鍍鎳層的微小硬度.....	45 4.1.3 光學顯微金相觀察.....
.....48 4.1.4 平面向TEM試片觀察.....	55 4.1.5 橫截面TEM試片觀察.....
.....62 4.2 PH值的影響.....	76 4.2.1 XRD組織觀察.....
.....76 4.2.2 鍍鎳層的微小硬度.....	76 4.2.3 光學顯微金相觀察.....
.....79 4.2.4 平面向TEM試片觀察.....	85 4.2.5 橫截面TEM試片觀察.....
.....85 4.3 氫離子的影響.....	98 4.3.1 XRD組織觀察.....
.....98 4.3.2 鍍鎳層的微小硬度.....	101 4.3.3 光學顯微金相觀察.....
.....105 4.3.4 平面向TEM試片觀察.....	114 4.3.5 橫截面TEM試片觀察.....
.....115 4.4 氫離子的影響.....	141 4.4.1 XRD組織觀察.....
.....141 4.4.2 鍍鎳層的微小硬度.....	144 4.4.3 光學顯微金相觀察.....
.....147 4.4.4 平面向TEM試片觀察.....	155 4.4.5 橫截面TEM試片觀察.....
.....156 4.5 銅/鎳界面、擴散層的觀察.....	181 4.6 鍍鎳層的磨耗試驗.....
.....184 第五章 討論.....	185 第六章 結論.....
.....189 第七章 展望.....	196 參考文獻.....
.....198 附錄一.....	203 自傳.....
.....206	

REFERENCES

- H. Brown and B. B. Knapf, in: Modern Electroplating 3rd, Electrochemical Society, 1974
- 李鴻年,張紹恭,張炳乾,宋子玉等編著, "實用電鍍工藝", 國防工業出版社, 1991, 154-203
- 蘇癸陽編譯, "實用電鍍理論與實際", 復文書局
- W. H. William, in: The Properties of Electrodeposited Metals and Alloys, 2nd (American Electroplaters and Surface Finishing Society, Florida), 1986, 253-325
- 陳志雄, "大鋼胚連續銅模鍍鎳研究", 技術與訓練, 中鋼研究發展報告, 1986, 11-19
- G. Maurin, A. Lavanant, "Electrodeposition of Nickel/Silicon Carbide Composite Coatings on Rotating Disc Electrode", J. of Applied Electrochemistry, Vol.25, 1995, 1113-1121
- F. K. Sautter, "Electrodeposition of Dispersion-Hardened Nickel-Al₂O₃ Alloys" J. of The Electrochemical Society, Vol.110, No.6, 1963, 557-560
- M. Verelst, J. P. Bonino and A. Rousset, "Electroforming of Metal Matrix Composite: Dispersoid Grain Size Dependence of Thermostructural and Mechanical Properties", Materials Science and Engineering, A135, 1991, 51-57
- G. A. Di Bari, "Nickel Plating", Vol.5, ASM Materials Handbook, 1994, 201-212
- Don Baudrand, "Nickel Sulfamate Plating, Its Mystique and Practicality", Metal Finishing, Vol.94, No.7, 1996, 15-18
- 彭裕民譯, "鍍鎳的基本溶液及工業電鍍的應用", Vol.64, 54-64
- Lowenheim, Fredeerick Adolph, "Electroplating", American Electroplaters' Society, McGraw-Hill, 1978
- S. K. Verma and H. Wilman, "The Structure and Crystal Growth of Nickel Electrodeposit From a Sulphamate Bath on Polished Polycrystalline copper, in Relation to Thickness, Rate of Deposition, Temperature and Stirring", J. Phys. D: Appl. Phys., Vol.4, 1971, 2051-2065
- S. Nakahara and E. C. Felder, "Defect Structure in Nickel Electrodeposits", J. Electrochem. Soc.: Electrochemical Science and Technology, Vol.129, No.1, 1982, 45-49
- G. Konishi, "Stress in Nickel Plating", Journal of the Metal Finishing Society of Japan, Vol.11, 1960, 263-268
- J. W. Dini and H. R. Johnson, "The Influence of Nickel Sulfamate Operating Parameters on The Impurity Content and Properties of Electrodeposits", Thin Solid Films, Vol.54, 1978, 183-188
- S. W. Banovic, K. Barmak and A.R. Marder, "Microstructure Characterization and Hardness of Electrodeposited Nickel Coatings From a Sulphamate Bath", Journal of Materials Science, Vol.33, 1998, 639-645
- 彭坤增, "銅模鍍鎳層組織及性質受熱潛熱之研究", 大葉大學機械工程研究所碩士論文, 1998
- B. E. Jacobson and J. W. Sliwa, "Structure and Mechanical Properties of Electrodeposited Nickel", Plating and Surface Finishing, Vol.60, No.9, 1979, 42-47
- R. Weil, W. N. Jacobus, Jr., and S. J. DeMay, "The Effect of Annealing on the Microstructure and Hardness of Some Nickel Electrodeposits", Journal of The Electrochemical Society, Vol.111, No.9, 1964, 1046-1052
- J. W. Dini, "Electrodeposition", The Materials Science of Coatings and Substrates, 1992
- Yasuhiko Kawanami, Masahiko Nakano, Masanori Kajihara and Tsutomu Mori, "Growth Rate of Fine Grains Formed by Diffusion Induced Recrystallization in Ni Layer of Cu/Ni/Cu Diffusion Couples", Materials Transactions, JIM, Vol.39, No.1, 1998, 218-224
- H. R. Johnson, J. W. Dini and R. E. Stoltz, "The Influence of Thickness, Temperature and Strain Rate on the Mechanical Properties of Sulfamate Nickel Electrodeposits", Plating and Surface Finishing, Vol.66, No.3, 1979, 57-61
- D. R. Cliffe and J. P. G. Farr, "Growth Habits of Electrodeposited Nickel and Cobalt", Journal of the Electrochemical Society, Vol.111, No.3, 1964, 299-306
- J. A. Crossley, P. A. Brook and J. W. Cuthbertson, "Electron-Microscope Studies of the Structure of Nickel Deposited in the Presence of Addition Agents", Electrochimica Acta, Vol.11, 1966, 1153-1161
- R. Weil and H. C. Cook, "Electron-Microscopic Observations of the Structure of Electroplated Nickel", Journal of the Electrochemical Society, Vol.109, No.4, 1962, 295-301
- M. Saleem, P. A. Brook and J. W. Cuthbertson, "Note on the Structure of Nickel Deposited from Sulphamate Solutions", Electrochimica Acta, Vol.12, 1967, 553-555
- S. Kaja, H.W. Pickering and W.R. Bitler, "Effect of PH on the Microstructure of Nickel Electrodeposits: A TEM Study", Plating and Surface Finishing, January, 1986, 58-61
- R. Weil, H. J. Sumka, and G. W. Greene, "Annealing Behavior of Fine-Grained Nickel Electrodeposits", J. Electrochem. Soc.: Electrochemical Science, Vol.114, No.5, 1967, 449-451
- J. Amblard, I. Epelboin, M. Froment and G. Maurin, "Inhibition and Nickel Electrocrystallization", Journal of Applied

Electrochemistry, Vol.9, 1979, 233-242 31.G. D. Hughes, S. D. Smith, C. S. Pande, H. R. Johnson and R. W. Armstrong, " Hall-Petch Strengthening for the Microhardness of Twelve Nanometer Grain Diameter Electrodeposited Nickel ", Metallurgica, Vol.20, 1986, 93-97 32.E. J. Suoninen, T. Hakkarainen, " Letters ", Journal of Materials Science, Vol.3, 1968, 446-448 33.D. N. Lee nad G. C. Ye, " Orientation and Microstructure of Watts and Bright Nickel Electrodeposits ", Plating and Surface Finishing, Vol.68, November, 1981, 46-50 34.A. Argyriou and N. Spyrellis, " Nickel Electrodeposition From All-Sulphate and All-Chloride Baths. Texture and Microhardness ", Trans. Inst. Metal Finish, Vol.71, No.3, 83-84 35.N. Atanassov, K. Gencheva and M. Bratoeva, " Properties of Nickel-Tungsten Alloys Electrodeposited from Sulfamate Electrolyte ", Plating and Surface Finishing, February, 1997, 67-71 36.F. J. A. DEN BROEDER, " Diffusion-Induced Grain Boundary Migration and Recrystallization, Exemplified by the System Cu-Zn ", Thin Solid Films, Vol.124,1985,135-148